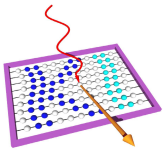

# Variational quantum Monte Carlo for ideal and relaxed surfaces of solids


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## Introduction

Variational quantum Monte Carlo (VMC) directly includes many-body effects at solid surfaces

- total energy optimization and variational principle
- exact Hamiltonian with full Coulomb interactions
- ab initio nonlocal pseudopotential
- correlated many-particle trial wave function $\Psi=\Psi_S\,\Psi_J$ of *Slater-Jastrow* type for up to 400 electrons
- parameterized localized orbitals in $\Psi_S$
- confinement term $v_{cf}$ in $\Psi_J$ variationally rules localization to the surface system
- thin film geometry with 8 resp. 12 layers (2x2 supercell, 256 resp. 384 electrons)
- comparison of two surface models of GaAs(110): ideal vs. Duke
- stepwise optimization: confinement ($V_{cf}$, $S_{cf}$) dangling bond s-p ($\zeta_s$, $\zeta_p$, $\gamma_p$) dangling bond angle ($\vartheta$)
- surface ion displacement ("phonon")

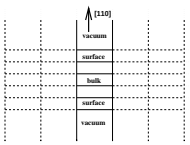
## Integration

Total energy as expectation value of the Hamiltonian by highdimensional stochastic integration over electronic degrees of freedom $\vec{Y}$
($\lambda$: set of variational parameters)

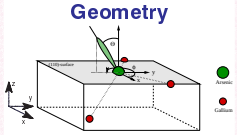
$$E_\lambda = \frac{\langle\Psi_\lambda|H|\Psi_\lambda\rangle}{\langle\Psi_\lambda|\Psi_\lambda\rangle} = \int \frac{|\Psi_\lambda(\vec{Y})|^2}{\int|\Psi_\lambda(\vec{Y})|^2\,d\vec{Y}} \frac{H(\vec{Y})}{\Psi_\lambda(\vec{Y})}\,d\vec{Y} \approx \frac{1}{M}\sum_{i=1}^{M} \frac{H(\vec{Y}_i)}{\Psi_\lambda(\vec{Y}_i)}, \quad \sigma_\lambda(E_\lambda) = \frac{1}{\sqrt{M}}\sqrt{\mathrm{Var}\frac{H\Psi_\lambda}{\Psi_\lambda}}$$

*Metropolis* algorithm for importance sampling of integration points

Boundary conditions of integration: 2D-periodic in the surface plane:

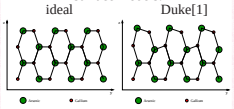



## Geometry




surface models:

ideal Duke[1]



## Hamiltonian

The Hamiltonian consists of:

+ kinetic energy,

+ nonlocal pseudopotential [2,3] (*Hamann-Schlüter*, d as local)

+ 2D-periodic Coulomb interactions like

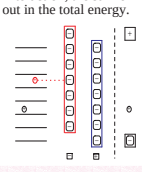
$$\sum_{\mathbf{R}_\parallel} \frac{Z_a Z_b}{|\mathbf{r}_a - \mathbf{r}_b - \mathbf{R}_\parallel|}$$

evaluated with 2D-*Ewald* summation technique and used per interpolation.

## Jellium

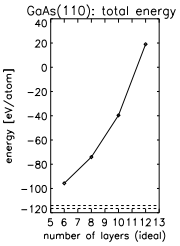
Divergent 2D-lattice summations brought to convergence by introducing a neutralizing background charge in each interaction, the sum of which cancels out in the total energy.

Splitting into symmetric part $v^s$ plus dipole part



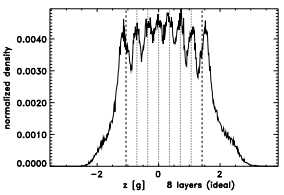
## Delocalization & finite size

Pure bulk-derived VMC scheme shows bad finite size behaviour:

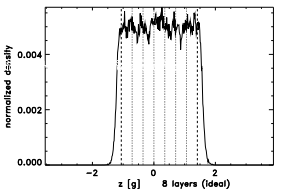



Explanation:

Electrons drift too far into vacuum regions due to repelling effect of the *Jastrow* factor, as shown by the z-resolved density:




Introduction of a confinement factor into the trial wave function leads to better, i.e. energetically more favourable, z-sampling:




## Wave function

The many-particle trial wave function $\Psi_\lambda$ with variational parameters $\lambda$ consists of two parts:

× The ***Slater*** determinant with parameterized localized orbitals $\phi_{\alpha\mu}$ (linear combination of 4s- and 4p-orbitals of Ga and As; $\alpha$: As-ion index, $\mu$: tetrahedral direction)

$$\Psi_\lambda(\vec{r}_1\sigma_1\ldots\vec{r}_N\sigma_N) = \Psi_S(\{\vec{r}_i\})\;\Psi_J(\{\vec{r}_{ij},\sigma_{ij}\},\{z_i\})$$

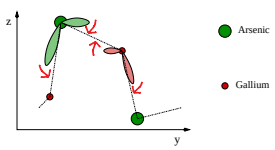
$$\Psi_S(\{\vec{r}_i\}) = \det(\phi_k(\vec{r}_i))\cdot D^\uparrow D^\downarrow$$

$$\phi_{\alpha\mu}(\vec{r}) = \phi^{\mathrm{As}}_{\alpha\mu}(\vec{r}) + \beta\,\phi^{\mathrm{Ga}}_{\alpha\mu}(\vec{r})$$

$$\phi^{\mathrm{DB}}_{\alpha\mu}(\vec{r}) = \phi^{\mathrm{As}}_{\mathrm{s}}(|\vec{r}-\vec{R}^{\mathrm{As}}_\alpha|/\zeta_s) + \gamma_{\mathrm{p}}\sum_{i=x,y,z}\tau^i_{\alpha\mu}(\vartheta,\phi)\;\phi^{\mathrm{As}}_{\mathrm{p}i}(|\vec{r}-\vec{R}^{\mathrm{As}}_\alpha|/\zeta_p)$$

Surface specific parameters are: $\zeta_s$, $\zeta_p$ (contraction), $\gamma_p$ (s-p-weight), $\vartheta$ (polar angle) in the dangling bond orbital.

The other p-orbital coefficients $\tau_{\alpha\mu}$ are adjusted automatically to relaxation:




× The ***Jastrow*** factor accounts for correlation ($u$, bulk parameter $A$) and confinement ($v_{cf}$, parameters $V_{cf}$, $S_{cf}$, $L_{cf}$):

$$\Psi_J(\{\vec{r}_{ij},\sigma_{ij}\},\{z_i\}) = \exp\Big(-\sum_{i<j}u(\vec{r}_{ij},\sigma_{ij})\Big)\times \exp\Big(-\sum_i v_{cf}(z_i)\Big)$$

$$u(\vec{r}_{ij},\sigma_{ij}) = A\Big(\frac{1}{r_{ij}}+v^s(\vec{r}_{ij})\Big)\Big(1-e^{-r_{ij}/F(\sigma_{ij})}\Big)$$

$$v_{cf}(z) = \frac{\epsilon V_{cf}}{2}\Big(\tanh\big(S_{cf}(z-z^c-\epsilon L_{cf})\big)+\epsilon\Big)$$

The two-particle term $\exp(-u)$ decreases when two particles come close to each other leading to a **smoothing** of the electronic density.

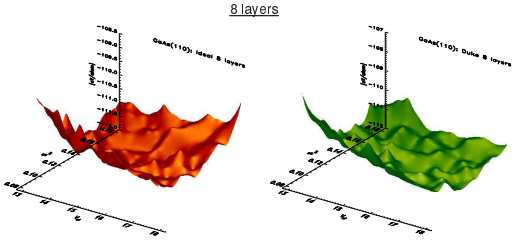
The confinement term $\exp(-v_{cf})$ rules the **localization** to the whole surface system.

## Confinement optimization

Total energy vs. confinement parameters $V_{cf}$, $S_{cf}$ for GaAs (110)

ideal surface — Duke surface

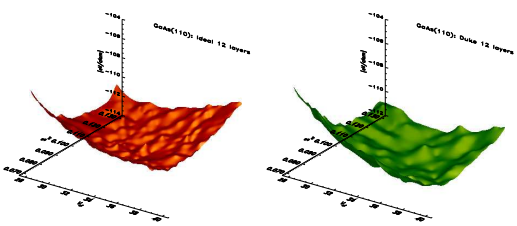
8 layers




$E_{8,i}$ = -111.46 eV/atom @ ($V_{cf}$|$S_{cf}$)=(15.3|0.139)

$E_{8,d}$ = -111.59 eV/atom @ ($V_{cf}$|$S_{cf}$)=(16.6|0.138)

12 layers



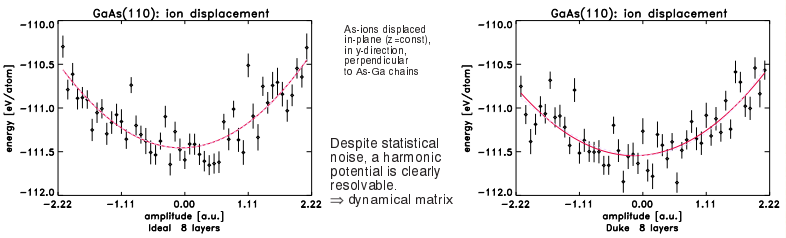

$E_{12,i}$ = -111.82 eV/atom @ ($V_{cf}$|$S_{cf}$)=(32.7|0.103)

$E_{12,d}$ = -111.80 eV/atom @ ($V_{cf}$|$S_{cf}$)=(34.5|0.103)

## "Phonons"

Test case: sensitivity to relaxation of surface ions?

ideal, 8 layers — Duke, 8 layers




As-ions displaced in-plane (z=const), in y-direction, perpendicular to As-Ga chains

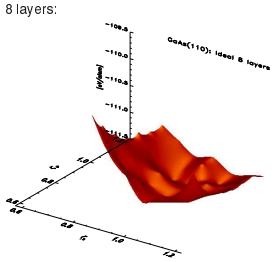
Despite statistical noise, a harmonic potential is clearly resolvable.
⇒ dynamical matrix

k = 0.42 eV/$(a_0)^2$ → ω = 11.9 meV ∗(1±0.09)

k = 0.36 eV/$(a_0)^2$ → ω = 10.4 meV ∗(1±0.09)

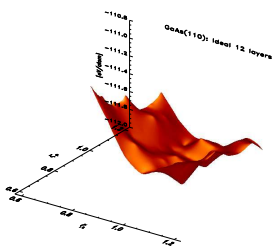
## Dangling bond: contraction

8 layers:



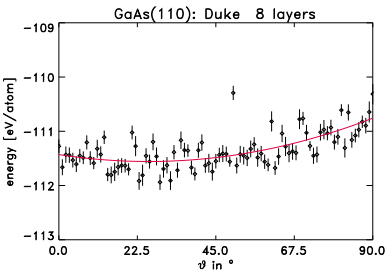

$E_{8,i}$ = -111.51 eV/atom @ ($\zeta_s$|$\zeta_p$)=(0.99|1.04)

12 layers:




$E_{12,i}$ = -111.81 eV/atom @ ($\zeta_s$|$\zeta_p$)=(0.97|1.15)

## Dangling bond: angle




$E_{8,d}$ = -111.55 eV/atom @ ϑ=26°

## Summary

! Bulk-derived VMC scheme shows poor finite size behaviour

! New confinement term gives much deeper total energy and better finite size behaviour

! Dangling bond properties resolvable

! Significant differences between Duke surface and ideal surface

! Surface ion relaxation shows harmonic dependence

## Outlook

! Full optimization and finite size analysis

! Determination of pair correlation function

! New information about exchange-correlation functional

## References


[1] C.B. Duke, S.L. Richardson, A. Paton, and A. Kahn: *Surf. Sci.* **127**, L135 (1983).

[2] S. Fahy, X.W. Wang, and S.G. Louie: *Phys. Rev. B* **42**, 3503 (1990).

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[4] R. Bahnsen, H. Eckstein, W. Schattke, N. Fitzer, and R. Redmer: *submitted to Phys. Rev. B*; s. *cond-mat/0008*



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